CHAPTER 20: CHEMICAL CLEANING OF BOILERS

Chemical cleaning is a very important aspect of boiler maintenance, not only for achieving a good clean, but also because **if it is not done correctly it can damage the boiler's metal and pose risks.**

Chemical boiler cleaning must be performed with sufficient knowledge of which chemical elements to use, which procedures are most appropriate, and with due regard for boiler safety and, above all, the safety of the operators performing the chemical cleaning.

Generally, two types of chemical cleaning can be performed on scaled boilers (if the boiler has not been chemically treated or the chemical treatment is of questionable effectiveness).

The first type we will show has three stages:

1st STAGE: alkaline stage,
2nd STAGE: acidic stage,
3rd STAGE: neutralization and passivation stage.

1st STAGE: alkaline stage

The first alkaline stage prepares the scaled surfaces for penetration by the acid to be used. This stage generally involves boiling with soda ash (and an anti-embrittlement agent), with a free soda content of approximately 2% to 4%.

This is done with 75% steam pressure for about 24 hours, purging the system and ensuring the steam is not used for the industrial plant's consumption.

The other chemical cleaning scenario is when the boiler is scaled, but its chemical treatment, while adequate, was insufficient at times.

Despite being a treated boiler, it allowed scale to accumulate from hard water that entered for various reasons (these scales are generally composed of calcium or magnesium carbonates).

In this case, the first alkaline stage is skipped, and the acid stage is used directly.

2nd STAGE: acidic stage

The most commonly used acid for chemical cleaning is **hydrochloric acid (HCl)**, due to its ease of handling and its strong ability to bind with carbonate deposits.

CAUTION: DO NOT USE HYDROCHLORIC ACID ON BOILER PARTS MADE OF CHROMIUM-NICKEL STEELS (generally high-temperature superheaters).

Several things need to be clear: acid, whatever its type, attacks iron metal unless an "acid inhibitor" is used (e.g., Rodine 60® or another). Formaldehyde was used in the past.

The second thing to keep in mind is that acid works best at a certain temperature (it hardly attacks scale when cold), so generally around 60-80°C (140-176°F).

The third consideration is the reaction time inside the boiler and the theoretical concentration of pure acid at the start of the acid treatment, the concentration it should have at the end, and the final concentration required to complete the acid treatment (which should never exceed 12 hours).

Another consideration is that the burner should not be lit under any circumstances during this acid treatment stage.

And very importantly: when acid attacks iron metal, it produces hydrogen gas (H2), a highly explosive gas, so it is essential to install a good vent (extractor/fan) for these gases at the top of the boiler (such as a connection from a safety valve to the chimney with a pipe of good diameter).

Regarding safety, at all stages, chemicals must be handled using appropriate personal protective equipment (PPE): safety glasses, acid masks, gloves, aprons, and rubber boots.

It is advisable to have a fan that strongly circulates the air in the chemical cleaning work area, and to include a hose with running water to wash away any chemical spills, whether on the floor, the boiler, or the operators themselves (in addition to having buckets of clean water readily available to immediately wash any part of the body that has come into contact with the acid).

It should also be considered that at each stage, the chemicals, previously neutralized, must be discharged into the wastewater discharges or effluent treatment plant of the industrial plant.

Since the first stage is alkaline (water with a high pH will be discharged), while the second stage is acidic, although the acid is consumed, it is generally discharged into the drain still with a certain concentration as pure acid (close to 1% if calculated correctly).

It is recommended that the acid cleaning should be done in about 12 hours and no more, since if it is done for longer, the metal is attacked microscopically, causing it to resemble a porous "pumice stone" (whose holes are not visible to the naked eye, but in a hydrostatic test, it will cause the pipes to "sweat" when subjected to the pressure of the test water for a reasonable time.

The neutralization of the effluents from the acid stage should be done outside the boiler (in a tank or reservoir of the blowdown pit) using the alkaline water from the first stage, if it was done, or using liquid soda or "quicklime" (previously dissolved).

3rd STAGE: neutralization and passivation stage

The third stage, a neutralization and passivation stage, should be carried out similarly to the first alkaline stage, raising the pressure to 75% of the working pressure (24 hours, purging every hour).

However, a passivating agent must be used to cause oxidation of the surfaces, reforming the **magnetic oxide layer** that protects the surface of the boiler tubes and allows a bare iron tube to last so many years.

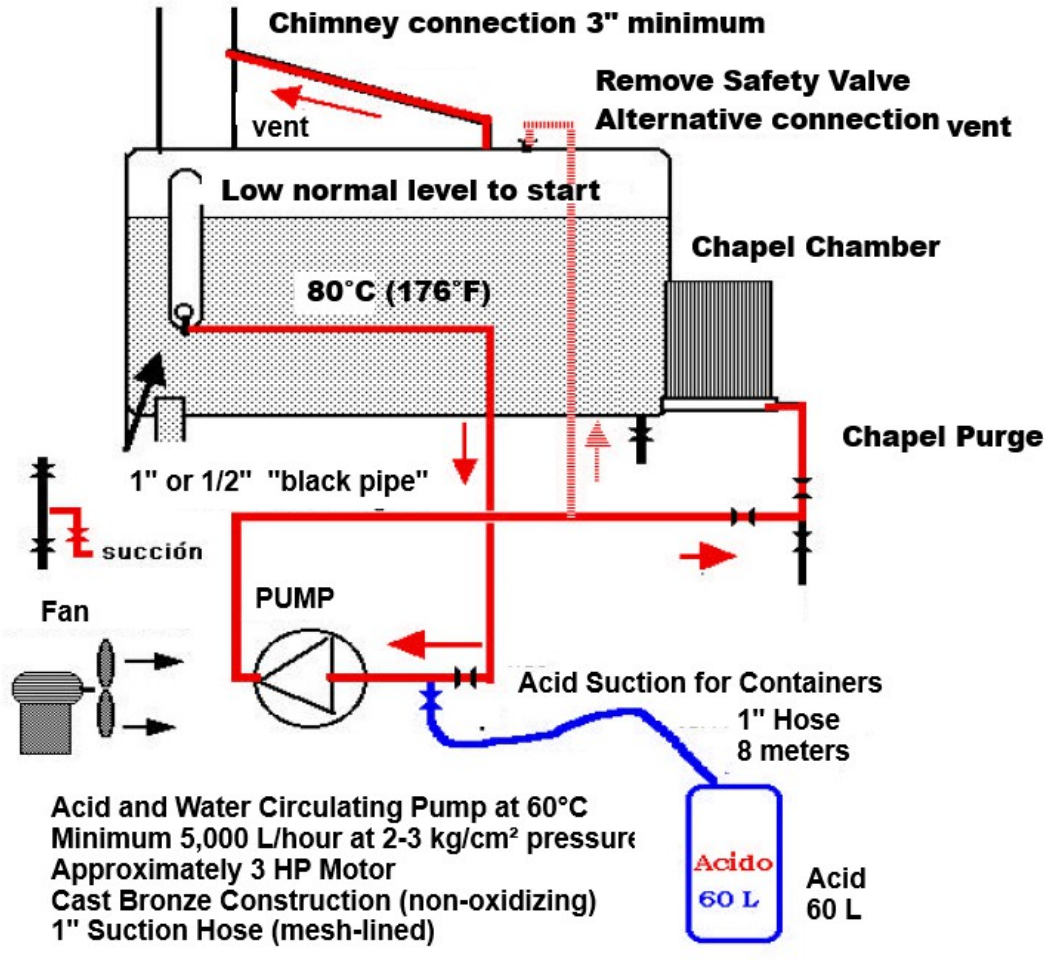
In some boilers, we have far exceeded 30 years and much more, to the point that the tubes wear out first on the flue gas side.

In the acid stage, it is generally assumed that there will be a theoretical need for 5% pure hydrochloric acid (15% commercial acid at 30%-34% HCl) and the inhibitor is usually 1% to 5% of the commercial acid (depending on the acid inhibitor used).

Hydrochloric acid (HCl) is a gas dissolved in water, so at high temperatures it will tend to escape from the water in which it is dissolved (hence the importance of the vents, fans, and masks used).

The preparation of the system, boiler and accessories, is fundamental, since it can be done very crudely by hand (acid from containers is added through the manhole) or more correctly (for safety) by means of acid pumps or simple circulation pumps (not made of stainless steel) that take water from the same boiler and discharge into another area of the boiler, with a connection to the suction that allows the acid to be drawn directly from the acid containers.

Let's look at the diagram:
The circulating pump is actually more than just for introducing the acid safely and easily; it doesn't need to run for the entire 12 hours of acid cleaning, since what actually circulates and agitates the acid inside the boiler are the "bubbles" (CO_2) released from the acid's attack on the carbonate scale..



As mentioned, the process starts with a water temperature between 60°C (140°F) and 80°C (176°F), preventing the burner from igniting with acid inside the boiler.

While the minimum amount of acid required is 15% commercial hydrochloric acid, we must consider that if the boiler is heavily scaled, we should have extra acid on hand to replenish it if, after adding the acid in approximately 1 to 2 hours, the concentration reaches 4% pure acid.

When the acid is first added, very violent reactions can occur between the acid and the scale, causing a rapid rise in the boiler water level due to bubbles.

This can sometimes be so violent that water can be expelled through the boiler openings (e.g., with the manhole cover open), soaking people and damaging equipment.

Therefore, the acid must be added slowly and carefully to prevent the level from rising too high (which is why the process begins with the boiler water level at its lowest point, but ensuring the tubes remain submerged).

To measure the HCL acid concentration, we use Methyl Orange (pH approximately 4.3) as a pH indicator and "titrate" with calibrated sodium hydroxide to a value appropriate to the sample size to obtain the percentage of pure hydrochloric acid.

N/1.33 sodium hydroxide directly yields 1% of acid as HCl for each cm^3 of sodium hydroxide consumed to change the Methyl Orange indicator to a percentage of pure acid when the sample being analyzed is approximately 5 cm^3.

For example: in a 5 cm^3 sample of boiler water diluted to 50 cm^3 with distilled water, a few drops of Methyl Orange are added, producing a dark, almost reddish color. When adding dropwise, while swirling in a Herlenmeyer flask with N/1.33 sodium hydroxide until the color changes to a nearly clear color, the volume of N/1.33 sodium hydroxide in cm^3 directly indicates the percentage of HCl.

Obviously, one must be very experienced in taking this measurement before the task of performing a chemical cleaning of the boiler with hydrochloric acid (HCl). This type of chemical cleaning cannot be improvised, as it poses a risk to people on duty there, and might damage the boiler itself.

The end of this acid stage is observed after approximately 9 hours. This is indicated by the agitation of the boiler water (the formation of CO2 bubbles). If the water is not agitated by these bubbles, it means that the acid's action on the scale is in its final phase.

The acid concentration is measured every half hour, and when it is the same concentration after a half-hour interval, this acid stage is considered complete.

Generally, if the amount of acid was calculated correctly, at the end of the operation the acid concentration will be 1% or less as pure HCl.

The operation should be completed in less than 12 hours, as continuing the acid process for longer will damage the boiler metal.

To dispose of the acid as effluent, remember to neutralize it (using soda ash or quicklime).

The danger at this stage is that in the final part of the operation, if the boiler is not properly vented, hydrogen gas (H2) can accumulate from the reaction of the acid with the boiler metal. This gas is highly explosive at low concentrations (while there is a lot of activity with CO2 formation, the danger is lower since it is diluted by the CO2).

That is why it is important to connect a gas exhaust system
from a safety valve to the chimney (which will create a good draft to vent the gases to the atmosphere).

Once the acid stage is complete, the inside of the boiler must be hosed down with water through the manhole.

Alternatively, the boiler should be filled and emptied approximately twice to remove residual acid from the walls, but primarily to remove the many deposits that the acid has released but not dissolved.

This stage must be carried out as quickly as possible to prevent oxidation in the presence of acid, which can cause significant corrosion (for example, if the boiler is left empty of acid in contact with the atmosphere for several hours).

The neutralization and passivation stage must be carried out immediately (using 2% to 4% soda ash for neutralization and passivating agents such as nitrites, borates, etc.).

The passivating agents form a new (very thin) protective layer of magnetic oxide on the iron metal surfaces.

Once the boiler has been inspected, it is filled with treated water and treatment chemicals, a hydraulic leak test is performed, and if everything is in order, the sealing gaskets are replaced, the covers are closed, the boiler is started up, and the covers and caps (which loosen under internal working pressure and heat) are retightened.

This operation must be carried out by someone with experience to avoid losing a cover or cap that could endanger the operator.

The safety of chemical cleaning must consider not only the operators involved, but all personnel who may be in the area (there are very irritating gases that, if not diluted and vented properly, contain hydrochloric acid as a gas, since hydrochloric acid is actually a gas dissolved in water, at its maximum commercial concentration it is 34% acid in water).

Although hydrochloric acid is not very aggressive to humans (in its liquid state, i.e., when the hydrochloric acid gas is dissolved in water), protective equipment must be used, especially respirators that absorb the acid (it greatly affects the respiratory tract because it is a highly irritating gas). Eyes should also be protected with appropriate goggles.

It is advisable to have a running hose with water available during acid operations and a bucket of clean water to wash off immediately if someone is affected by the acid. An eyewash station should also be available in case of splashes in one or both eyes, even if protective goggles are worn.

Since the eyes are very sensitive, even if they are washed immediately with clean water, irritation may remain, requiring an ophthalmologist's attention.

If the respiratory tract is affected, one should move to areas with uncontaminated air for minor irritations. Medical attention is necessary if the irritation is more severe.

Especially in sensitive people, such as asthmatics, whom we advise against doing these types of tasks.

Caution is advised when using caustic soda (sodium hydroxide flakes or pearls), as it can rapidly irritate the skin and eyes.

If contact occurs, wash immediately with water and seek medical help.

It is best to use caustic soda already diluted to 50% (liquid soda) or soda ash, which are less aggressive.

Adding caustic soda to water also releases highly caustic fumes that affect the respiratory system.

Therefore, it is essential to add the soda to the water (not the water to the soda) in a well-ventilated area (with a fan) and while wearing appropriate protective gear (goggles, masks, gloves, etc.).

If you are inexperienced with these procedures, it is advisable not to attempt them without professional assistance (from someone knowledgeable in the subject).

CHEMICAL CLEANING EXAMPLE:

Chemical cleaning of boiler (15 Ton/h, 12 Kg/cm2 = 172 PSI) scaled by use of "mixture" of well water and surface water (the operator loses track of the water quality and with it the regeneration rate of the water softener and the proper dosage of chemicals).

ESTADO DE LA CALDERA ANTES DE LIMPIAR

ESTADO DE LA CALDERA DESPUES DE LIMPIAR

URUMAN Conference, 17 noviembre 2022
(Uruguayan Society of Maintenance, Asset Management)
recognition to CWT for the authorship of the "Pequeño Manual del Foguista"
and ffor the training of boiler stokers in Uruguay (1980..2010).